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Solidification/Stabilization of Dyeing Sludge Treated by Fenton Reagent Using Blast Furnace Slag and Fly Ash

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This study was performed to reuse the dyeing wastewater sludge treated by Fenton process through the solidification/stabilization technique. To solidify the dyeing sludge the industrial by-products such as blast furnace slag, fly ash and waste sand with cement were used. The laboratory scale and pilot scale test were conducted at room tempertature to make construction brick which has high compressive strength and low leaching of heavy metals.

The experimental results showed that blast furnace slag and fly ash could be used instead of cement and the products satisfied the regulation of Korean Standards. The blast furnace slag increased the compressive strength and the optimum ratio of slag/dyeing sludge on dry basis was found 0.4. The solidifying agent of SB series could increase rapidly the compressive strength and the optimum ratio of solidifying agent/sludge on dry basis was 0.26 at which the strength was two times compared with non-added condition. The portion of waste and industrial by-products in matrix was over 80%. From the pilot test the optimum pressure in molding was 100kg$_f$ at which the compressive strength was over 100kg/cm^2. And the strength increased continuously to 160kg/cm^2 until 120 days curing time due to pozzolanic reaction.

When SB-20 as a solidifying agent was used, the unconfined compressive strength of dyeing sludge could be obtained 110kg/cm^2 which satisfied the regulation of cement brick in Korea Standard(KS).

I . INTRODUCTION

A lot of wastes and wastewater have been generated from households and industries. Especially, the textile industrial plants need a lot of process water and their wastewater contains high colority and refractory materials hard to degrade by normal activated sludge processes. Therefore the advanced treatment

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processes have been applied to treat the dyeing wastewater which contains various dyes and organic compounds with high pH and high temperature. Among many kinds of advanced treatment processes, Fenton process has been widely used in which hydrogen peroxide and ferrous salts are used as oxidant and catalyst.

The sludge produced in textile wastewater treatment plants increased and disposed in landfills or ocean disposals. But landfill sites are so insufficient and it is difficult to find new sites in Korea and ocean disposal could be expected to be prohibited. For the alternative treatment of sludges instead of landfill or disposal, incineration, solidification and high temperature pyrolysis methods could be used. The dyeing sludge treated by Fenton process contains low organic fraction and low heavy metals. Therefore the solidification/stabilization method seems to be very useful in the point of technical and economical view.

Cement-based solidification/stabilization is one of the preferred chemical treatment techniques for inorganic hazardous wastes, such as plating sludge and dyeing sludge. In the B textile dyeing plant complex in Korea, the wastewater sludge has been largely generated 66,500ton/year and 180~200ton on the daily basis. And blast furnace slag and waste sand also produced 34,721ton/day and 4,295ton/day, respectively in 1999.

This investigation was carried out to study the solidification/stabilization of dyeing wastewater sludge treated by Fenton process from the textile dyeing industrial complex for the reuse in construction field. To solidify the dyeing sludge the blast furnace slag, fly ash and waste sand with cement were used which byproducts were obtained from steel and power plants. In order to obtain high compressive strength and low leaching of heavy metals, various solidifying agents were used which were developed in our laboratory. The experiments were conducted in the laboratory scale and pilot plant scale at room temperature to satisfy the regulation for the construction brick (A type concrete $82kg/cm^2$).

II. MATERIALS AND METHODS

1. Experimental materials

Dyeing sludge used in this experiment was obtained from B textile wastewater treatment plants. Blast furnace slag and waste sand etc. were industrial by-products from P and I steel industrial plants. These materials can be used as binder or pozzolanic materials to enhance the solidification properties.

The raw dyeing sludge was dried at 100~105℃ in dry oven for 2 days. After that, the sludge was ground by ball mill and screened with 25 mesh sieve. Table 1.1 and 1.2 show the properties of dyeing sludge treated by Fenton reagents and its heavy metal concentrations. This shows that inorganic fraction was more than organic fraction. The iron content was the major constituent among heavy metals and the concentration of hazardous heavy metals was very low. The waste sand from foundry was dried and sieved under the size of 0.8mm. Fly ash from power plant was directly used as it was. The ordinary portland cement (OPC) was made in S cement co. Solidifiers such as SB series were composed of lime, alumina and others.

Table 1.1 Properties of Dyeing Sludge Treated by Fenton Reagents (unit : %)

pH	organics	inorganics	moisture
7.7	44.6	55.4	73

Table 1.2 The Concentration of Heavy Metals Contained in Dyeing Sludge (unit : %)

Fe	Cu	Pb	Cd	Hg	Al	Etc.
29	0.09	0.01	ND	0.05	1.0	4.8

2. Experimental methods

(1) Lab-scale experiment

Various matrix formulations were studied as shown in Table 2.1. The dried sludge was homogeneously mixed with cement, water and other additives using a mortar mixer for 10 min. The water contents was controlled in the range of 0.6~1.0 as W/C. The cubic molds (5cm×5cm×5cm) were used for making specimens with Korean Standard (KSF 5105). After 1~2 days, the cured specimens were demolded and were cured for 7, 14 and 28 days, respectively, at 25℃ in the humidity chamber.

The unconfined compressive strengths (UCS) were measured by UTM(Universal Test Machine, Instron Model 4201). SEM analysis and leaching test were conducted for the specimens after measurements of UCS. The leaching heavy metals were measured according to the KSLT(Korea) and TCLP(USA). The heavy metal contents such as Cd, Cu, Pb, Zn and Fe were analyzed by atomic absorption spectrophotometer.

(2) Pilot scale experiment

Pilot scale experiment was conducted in B dyeing wastewater treatment plant in

Table 2.1 The Matrix of Mixing for Solidification of Dyeing Sludge (Dry Basis).

Test	The Mixing ratios of compounded matrials (%)							
	Sludge	Cement	Solidifer	CaO	Sand	Fly ash	Slag	Other
T-1	50	12	-	13	10	10	5	-
T-2	45	12	-	13	10	10	10	-
T-3	40	12	-	13	10	10	15	-
T-4	35	12	-	13	10	10	20	-
N-1	50	12	-	13	5	10	10	-
N-2	45	12	-	13	10	10	10	-
N-3	40	12	-	13	15	10	10	-
N-4	35	12	-	13	20	10	10	-
SB-1	33	12	2.5	10.5	17.5	8	16.5	-
SB-2	33	12	4.5	8.5	17.5	8	16.5	-
SB-3	33	12	6.5	6.5	17.5	8	16.5	-
SB-4	33	12	8.5	4.5	17.5	8	16.5	-
SB-0	33	12	-	13	17.5	8	16.5	-
SB-8	33	12	8.5	4.5	17.5	8	16.5	-
SB-20	33	12	8.5	4.5	17.5	8	16.5	-

* SB (Solidifier) , Sand : Waste Sand , Sludge : Dyeing sludge

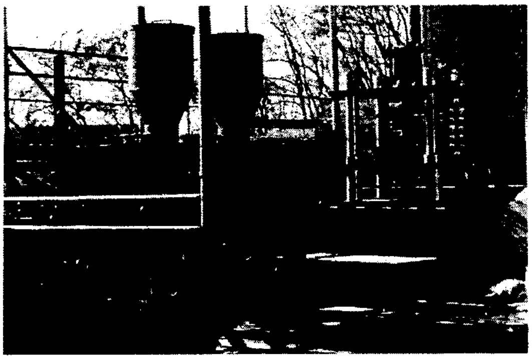

Fig. 2.1 A photograph of pilot plant

which pilot plant was installed. Fig. 2.1 illustrated the photos for the pilot plant. Dyeing sludge was wind-dried at the on-site and used without grounding because of mixing system in pilot plant. The sludge was mixed with blast furnace slag, fly ash, waste sand and solidifier etc. in the mixing system with control of water content. Specimens were made using press machine (oil press) in which the pressure was changed in the range of 50~300kgf. The measurements of UCS and heavy metal concentrations were as same as in lab-scale test.

Ⅲ. RESULTS AND DISCUSSIONS

1. Effect of blast furnace slag and waste sand on solidification

Blast-furnace slag was industrial by-product which is known to have the pozzolanic effect. When blast-furnace slag was used in the range of 5-20% on the dry basis, the relationship between unconfined compressive strengths and slag ratios (slag/dry sludge = 0.1 ~ 0.6) was shown in Fig 3.1. The compressive strength increased with the ratio of blast-furnace slag until the ratio 0.4. The highest compressive strength was 23.5 kg/cm^2 at slag/dyeing sludge = 0.4. But in the case of slag/sludge = 0.6, the compressive strength decreased compared with that of ratio 0.4 and the cracks of specimen was appeared. It seems that cracks was formed from the rapid hydration reaction and heat generated during reaction because of excess concentration of CaO in the mixture. The blast-furnace slag contained CaO 42%, Al_2O_3 16% and SiO_2 35% etc. From this result, the optimum dosage ratio of the blast-furnace slag was existed and it seemed to be about 0.4 (15%) of slag/sludge ratio.

Fig. 3.2 showed the change of compressive strength with the waste sand/sludge ratio. The compressive strength increased with sand/sludge ratio. It means that the compressive strength can be increased with decrease of dyeing sludge added. For the effective solidification/stabilization of dyeing sludge, the maximum dosage of waste sand was fixed at sand/sludge = 0.6.

2. Solidifying agents

In order to make stable and safe products which can show the high compressive strength, the new solidifying agents and additives have to be developed. A lot of additives were tested and various formulas were investigated to obtain higher compressive strength. As solidifying agents, SB series showed good results which were formulated in our laboratory.

To find the optimum ratio of SB series and solidifying agent, SB/sludge ratios were changed for several SB series. The experimental results for the varying SB/sludge ratios were shown in Fig. 3.3 in the range of SB/sludge ratio = 0.08 ~

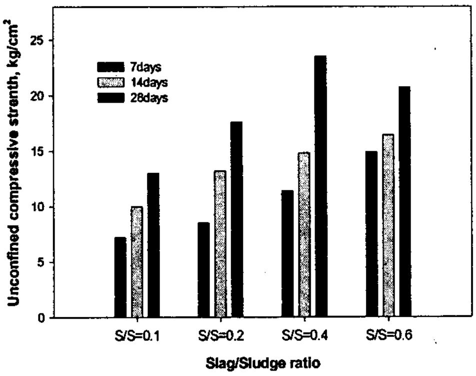

Fig.3.1 Changes of unconfined compressive strength with various Slag/dry sludge mixed ratios. (T-1, 2, 3, 4)

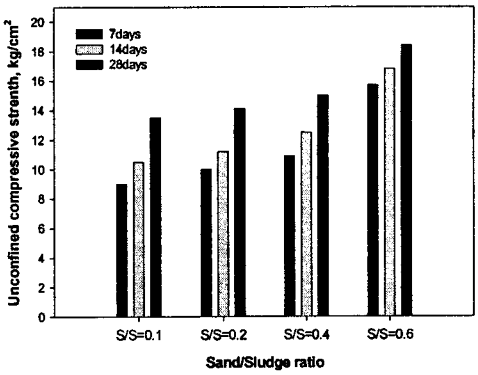

Fig.3.2 Changes of unconfined compressive strength with various Sand/dyeing sludge mixed ratios. (N-1, 2, 3, 4)

0.26 with the curing time. In the condition of the SB/sludge ratio 0.2, the compressive strength was very low. But in case of the SB/sludge ratio 0.26, compressive strength increased rapidly up to 45kg/cm^2 and 70 kg/cm^2. From these results, the addition of solidifying agent could increase the compressive strength and the optimum ratio of SB/sludge was found 0.26.

Fig. 3.4 showed the changes of compressive strength with the curing time at SB/sludge 0.26 for the added and non-added condition of solidifying agent.

When SB-20 was used as solidifying agent, the highest compressive strength could be obtained over 90kg/cm^2 at 28 days. This result shows that the compressive strength of specimen was over the Korean concrete brick regulation (82kg/cm^2). At the long term curing time

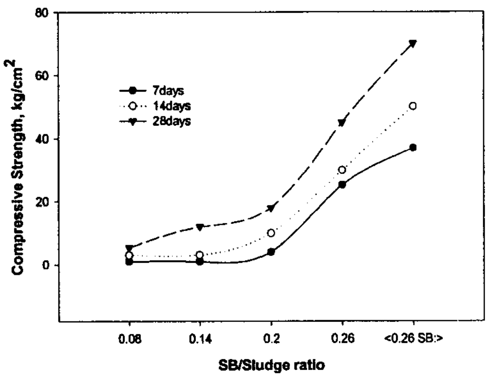

Fig. 3.3 Changes of unconfined compressive strength with various SB/ dry-sludge mixed ratios.

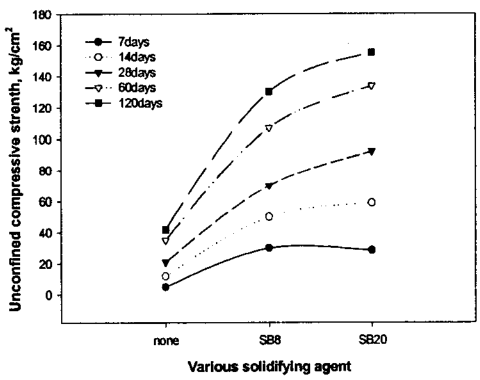

Fig. 3.4 Changes of UCS with different solidifying agent.

of 120 days, the compressive strength could be increased up to 160kg/cm^2. It shows that the pozzolanic reaction was proceeded continuously by the pozzolanic materials such as blast-furnace slag and fly ash etc.

From the microstructural analysis by SEM showed that a large number of crystalline products were formed. It was thought that ettringite was produced during the reaction.

3. Leaching test

The main heavy metals contained in the dyeing sludge were Cd and Fe. The leaching experimental results was shown in Table 3.1. As compared with raw sludge, all of the concentrations were lower than regulation limits. It means that high compressive strength could decrease the elution concentration of heavy metals and show a stable state.

Table 3.1 Leaching tests of solidified samples for the heavy metals.(TCLP) unit : mg/L

Item	T-Cr	Cu	Cd	Zn	Pb	Fe
SB4	0.015	0.125	ND	0.088	ND	0.379
SB8	0.009	0.104	ND	0.078	ND	0.349
SB20	0.005	0.01	ND	0.008	ND	0.05

* ND : Not detected

4. Pilot plant experiments

The compressive strength in the pilot test showed much higher by solidifying agent compared with non-addition case. The compressive strength at 28days increased up to 110kg/cm^2 which was higher than that of bench-scale test.

The experimental results for the various pressure applied in the forming were shown in Fig 3.5. From this result, the optimum pressure applied was found to be around 100kg$_f$.

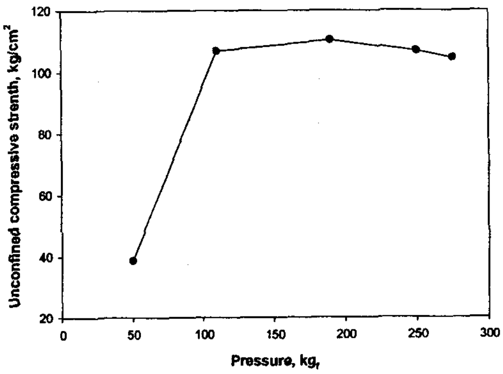

Fig. 3.5 Change of UCS with different pressure.

Ⅳ. CONCLUSIONS

From the experiments of the lab-scale and pilot scale for the reuse of dyeing sludge, the blast furnace and fly ash etc was found to be useful to solidify the dyeing sludge. The optimum ratio of blast furnace and solidifying agents were found.

The compressive strength could be obtained up to 110kg/cm^2 at 28 days of curing time which satisfied Korean concrete brick regulation. Also it showed very low leaching phenomena.

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